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Multi-electron Redox-based Organic Batteries

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Abstract

The electroactive organic compounds, e.g., 1,3-bis(4,4,5,5-tetramethylimidazolin-1-yl)oxy-3-oxide-2-yl)benzene, 1,4-bis(4,4,5,5-tetramethylimidazolin-1-yl)oxy-3-oxide-2-yl)benzene, phenazine-9,10-dioxide, triquinoxalinylene, tetraketopyracene and rubeanic acid have been tested as a cathode-active materials in rechargeable batteries. The multiple redox peaks in the cyclic voltammograms of the present compounds have been observed, indicating the multi-electron redox reactions. In galvanometric charge and discharge experiments of the half cell setup vs. Li, the high discharge capacities more than 400 Ah/kg were obtained, which exceeded those delivered by the conventional Li-ion battery. These results indicate that the multi-electron redox-based organic batteries are one of the promising candidates for the higher energy batteries.

1. INTRODUCTION

With the aim of realizing a more affluent world in the future a wide variety of intelligent devices, electric vehicles and smart energy management systems will be widely spread over all corner of society. Energy devices are increasingly becoming a part of the sophisticated input that is supporting this trend. However, the current technology of the lithium ion batteries using inorganic transition metal oxide as the cathode materials face serious problems relating to no growth in capacity as well as safety and resource costs in recent years.

Organic electrode-active materials provide an inherently novel approach to the advanced rechargeable batteries.^{1,2} Because of the structural diversity of organic compounds, there are numerous electro-active organic compounds compared with inorganic active materials.³⁻¹⁰ Recently organic radical batteries using stable nitroxide radical polymers as cathode-active materials have realized, which would be quickly chargeable and have a high power density.¹¹ However, the theoretical capacities of the stable radicals (111 -135 Ah/kg)¹² are much lower than that of

the conventional inorganic cathode materials (LiCoO₂) of 150 Ah/kg.

To increase the capacity of the batteries, we have been interested in the multi-electron redox systems as charge and discharge reactions.. Here we report the multi-electron redox-based organic battery using a variety of electro-active organic compounds as cathode materials.

2. EXPERIMENTAL

The molecular structure of the examined electro-active compounds, 1,3-bis(4,4,5,5-tetramethylimidazolin-1-yl)oxy-3-oxide-2-yl)benzene (*m*-DNNR), 1,4-bis(4,4,5,5-tetramethylimidazolin-1-yl)oxy-3-oxide-2-yl)benzene (*p*-DNNR), phenazine-9,10-dioxide, triquinoxalinylene, tetraketopyracene and rubeanic acid are shown in Fig.1. *m*-DNNR, *p*-DNNR and phenazine-9,10-dioxide, were synthesized by Prof. T. Koizumi of Kobe City College of Technology and Dr. Y. Miura. Triquinoxalinylene, was provided from Prof. T. Sugimoto of Osaka Prefecture University and Mr. T. Matsunaga of Nard Institute. Tetraketopyracene was provided Prof. S.

Aonuma of Osaka Electro-communication University.
Rubeanic acid was purchased and used without further purification.

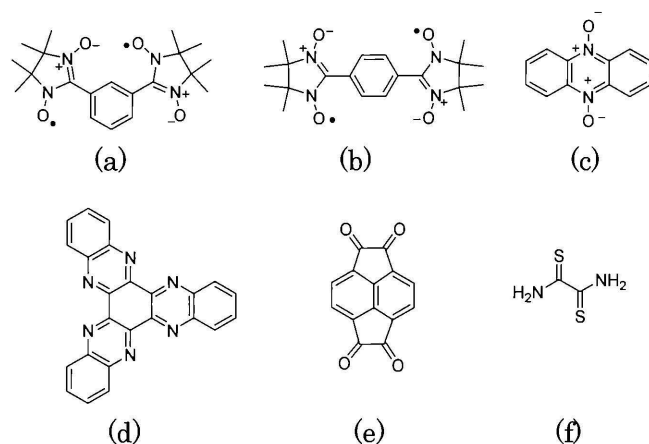


Fig. 1 Chemical structure of *m*-DNNR (a), *p*-DNNR (b), Phenazine-9,10-dioxide (c), triquinoxalinyne (d), tetraketopyracene (e) and rubeanic acid (f).

Electrochemical properties were measured using coin type half cell which fabricated by stacking cathode and Li-metal anode with porous polyolefin separator films. A cathode was formed by pressing the composites of the organic electrode-active material (10 wt.%), carbon fiber (80 wt.%), and fluorinated polyolefin binder (10 wt.%) as described in a previous paper.¹ The two kinds of the solution, i.e., a composite solution of ethylene carbonate (30 vol.%) and diethyl carbonate (70 wt.%) containing 1 M of LiPF₆ (LiPF₆/EC-DEC), and tetraethylene glycol dimethyl ether containing 4.8 M LiN(SO₂CF₃)₂, (LiTFSI/tetraglyme) were used as an electrolyte. Cyclic voltammograms (CV) were measured on a HOKUTO DENKO HSV-100 at a scan rate of 0.33 mV/s in the voltage range of 1.5– 4.2 V (vs. Li/Li). The garvanometric charge and discharge experiments were carried out at 25 °C using a computer controlled automatic battery charge and discharge instrument KIKUSUI PFX2011 in the voltage range of 1.5 – 4.2 V under constant current density of 0.088 mA/cm².

3. RESULTS AND DISCUSSION

3.1 *m*-DNNR and *p*-DNNR

The theoretical capacities of *m*-DNNR and *p*-DNNR is calculated to be 552 Ah/kg in terms of 8-electron reactions. Figure 2 shows the charge and discharge curves of *m*-DNNR cell fabricated with LiPF₆/EC-DEC as an electrolyte. After the initial charging of one-electron oxidation of the radical (110 Ah/kg), discharge process of one-electron reduction occurred at around 3.5 V followed by two- or three-electron reduction at around 2.6 V. The initial discharge capacity of 550 Ah/kg is remarkably larger than that of the conventional batteries and is close to the theoretical one.

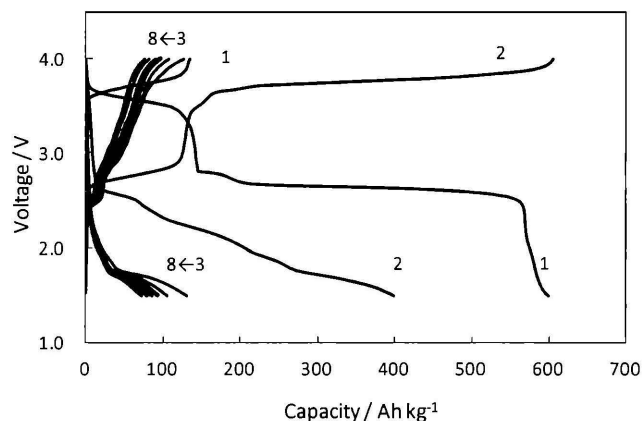


Fig. 2 Charge and discharge curves of *m*-DNNR half cell. Electrolyte: LiPF₆/EC-DEC.

After the second cycle, the voltage plateaus in discharge curves are completely destructed, and the capacity decreased significantly with the increasing cycle number. The electron spin resonance measurements of the electrode of the cell at various charging and discharging states indicated that the irreversible reactions occurred at the second charging process. It is likely that the reduced form like anion (Fig. 3(b)) or radical dianion (Fig. 3(a)) is unstable, reacting irreversibly to convert electrochemically inactive materials.

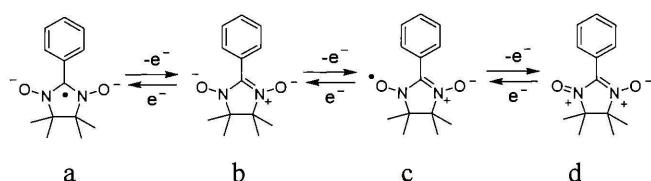


Fig. 3 Possible redox reaction of nitronyl nitroxide radical.

The radical generated by the reduction (Fig. 3(a)) the unpaired electron is delocalized over the molecule through pi-conjugated system. Accordingly, in *p*-DNNR the two unpaired electrons can couple to convert to a stable nonradical compound. On the other hand, such a coupling cannot occur for *m*-DNNR. In Fig. 4 the discharge curves of *p*-DNNR (first and second cycles) and *m*-DNNR (second cycle) are shown. In the case of *p*-DNNR the voltage plateau at 3.6 V observed at the first cycle is still kept, though the length is ca a half that at the second cycle. In the case of *m*-DNNR, on the other hand, the corresponding plateau is vanished. From these results, the coupling between the unpaired electrons via the pi-conjugated system may be partially effective for increasing stability. Although the satisfactory reversibility in the charge and discharge process was not observed for all nitronyl nitroxide radicals, a better reversibility could be achieved by proper selection of electrolyte and solvent.

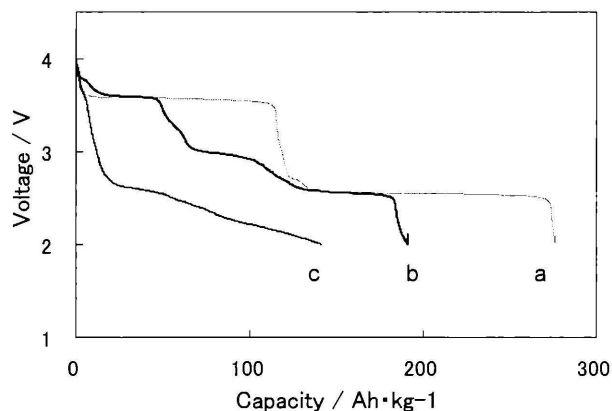


Fig. 4 Discharge curves of *p*-DNNR and *m*-DNNR half cell. a: *p*-DNNR 1st cycle, b: *p*-DNNR 2nd cycle, c: *m*-DNNR 2nd cycle. Electrolyte: $\text{LiPF}_6/\text{EC-DEC}$.

Figure 5 shows the charge and discharge curves of *m*-DNNR with $\text{LiTFSI}/\text{tetraglyme}$. Although the first discharge capacity reduced to 270 Ah/kg, the curves change in a similar form with cycling. Considering the dissolution of *m*-DNNR to the electrolyte solution, irreversible reactions should not occur in this system.

We have observed the multi-electron redox reactions for nitronyl nitroxide radicals. The maximum reversible capacity of 270 Ah/kg is slightly higher than that of the conventional Li-ion batteries.

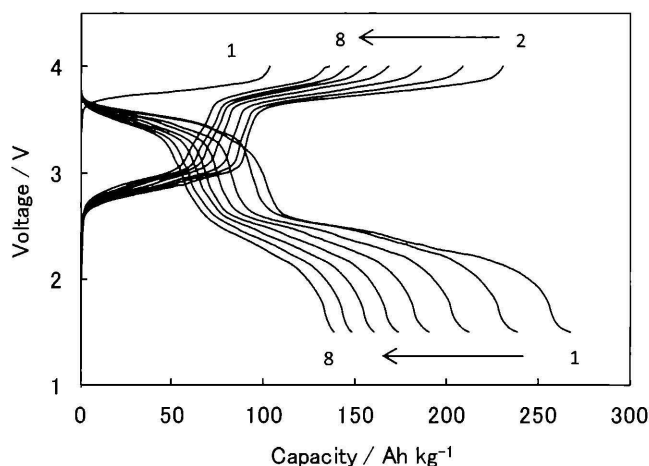


Fig. 5 Charge and discharge curves of *m*-DNNR half cell. Electrolyte: $\text{LiTFSI}/\text{tetraglyme}$.

3.2 Phenazine-9,10-dioxide

The discharge curves of phenazine-9,10-dioxide changed dramatically with cycling. That is, the initial capacity of 900 Ah/kg decreased to 240 Ah/kg at the second cycling. Moreover, we observed a gradual increase in the capacity after 2 cycles (Fig. 6). The analyses of the discharged electrode indicated the reaction of phenazine-9,10-dioxide with dimethyl carbonate in the electrolyte in the first charge and discharge processes. This reaction accelerated under high temperature.

The CV of phenazine-9,10-dioxide cell is depicted in Fig. 6. The product generated by the reaction of phenazine-9,10-dioxide with dimethyl carbonate after

10 cycles exhibited a redox potential at around 2.9 V.

Due to the formation of electro-active species during charge and discharge process, phenazine-9,10-dioxide showed the excellent stability in cycle performance. Namely, no significant deterioration in the capacity was observed for the phenazine-9,10-dioxide cell. Namely, the cell could still maintain a capacity as high as 250 Ah/kg even after 3000 cycles.

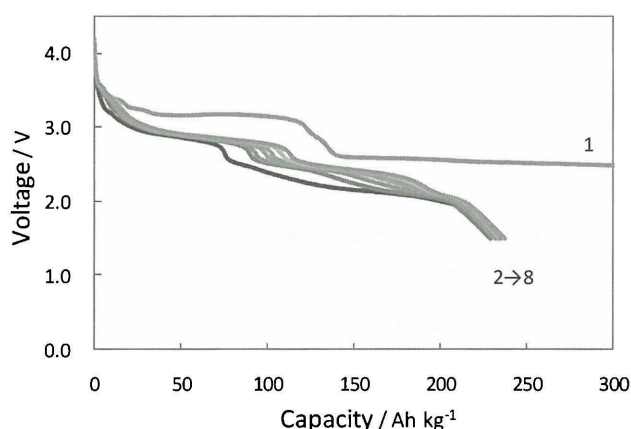


Fig. 6 Discharge curves of phenazine-9,10-dioxide half cell. Electrolyte: $\text{LiPF}_6/\text{EC-DEC}$.

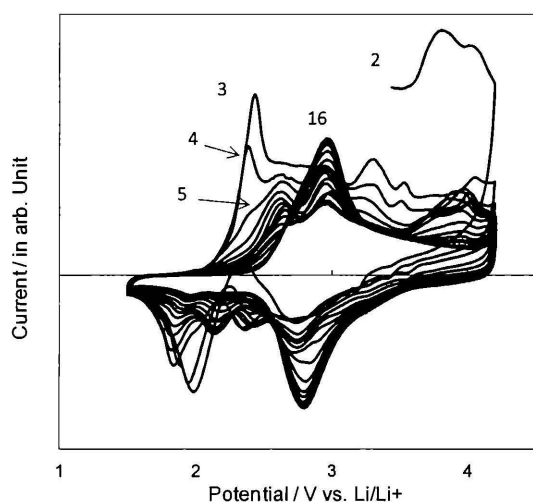


Fig. 7 Cyclic voltammograms of phenazine-9,10-dioxide.

3.3 Triquinoxalynylene

Assuming that triquinoxalynylene contribute to 6-electron reaction, we can estimate the theoretical capacity to be 418 Ah/kg. Figure 8 shows the charge

and discharge curves of triquinoxalynylene cell. Due to the charged state at the initial, the first charging capacity was very small. In the discharge process, two electron reduction occurred at 2.3 V followed by four electron reduction at 1.5 V. The experimentally observed discharge capacity of 420 Ah/kg was close to the theoretical one. The discharge capacity decreased with increasing the cycle number, which indicates the irreversible reactions or gradual dissolution of the active material into the electrolyte solution.

On the other hand, relatively characterless profiles are observed for charge curves. This seems to be due to the difference in the conductivity or reaction rate of triquinoxalynylene between charge and discharge processes.

Although there are problems in cycle stability, we have observed a high capacity of 420 Ah/kg with multi electron reaction for triquinoxalynylene.

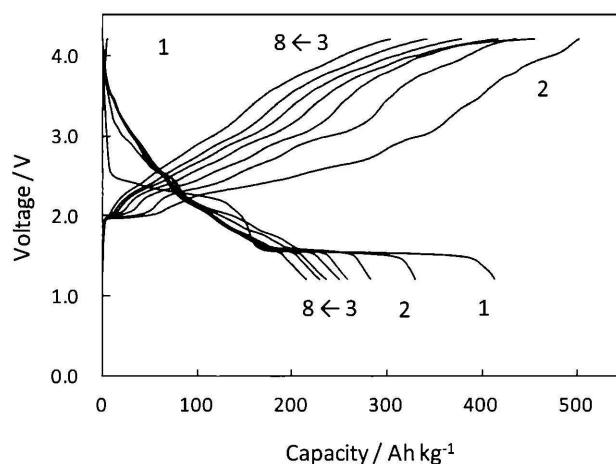


Fig. 8 Charge and discharge curves of triquinoxalynylene half cell. Electrolyte: $\text{LiPF}_6/\text{EC-DEC}$.

3.4 Tetraketopyracene

Tetraketopyracene possess two ortho-quinoid parts in a molecule and theoretical capacity of 458 Ah/kg. Figure 9 shows the charge and discharge curves of tetraketopyracene. Two-step discharging and charging processes are clearly observed in the first

discharge and second charge with voltage plateaus at around 2.7 V and 3.1 V. The capacity observed at first cycle is consistent with the theoretical one.

After the second cycle, voltage plateaus in discharge curves are completely destructed. An irreversible reaction seems to be occurred up to the second discharge. There exists a problems in cycle stability, the cell showed relatively higher capacity and output voltage. If we find the solution to increase the stability, tetraketopyracene should be a major candidate for the active material of next high energy batteries.

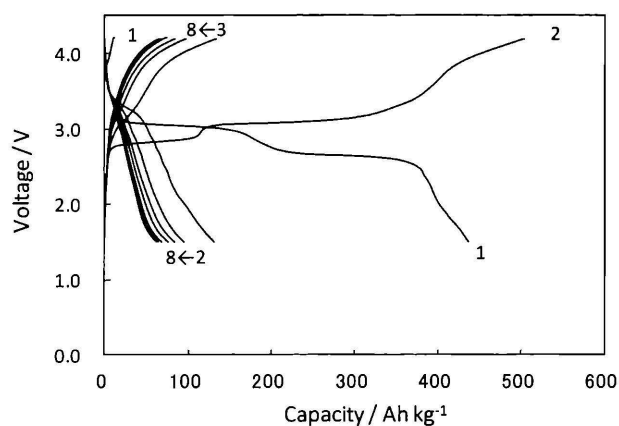


Fig. 10 Charge and discharge curves of tetraketopyracene half cell. Electrolyte: $\text{LiPF}_6/\text{EC-DEC}$.

3.5. Rubeanic acid

The use of small organic molecules as the cathode active material is one of effective approaches to an increases in the capacity. In this regard, rubeanic acid has a relatively high theoretical capacity of 445 Ah/kg calculated as the two electron reaction. Figure 11 shows the charge and discharge curves of rubeanic acid.

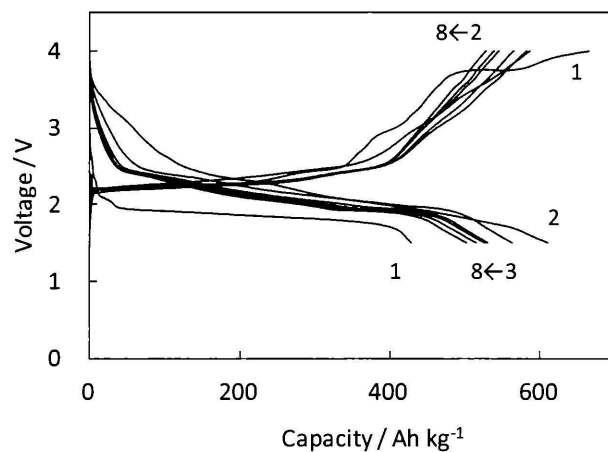


Fig. 11 Charge and discharge curves of rubeanic acid half cell. Electrolyte: $\text{LiTFSI}/\text{tetraglyme}$.

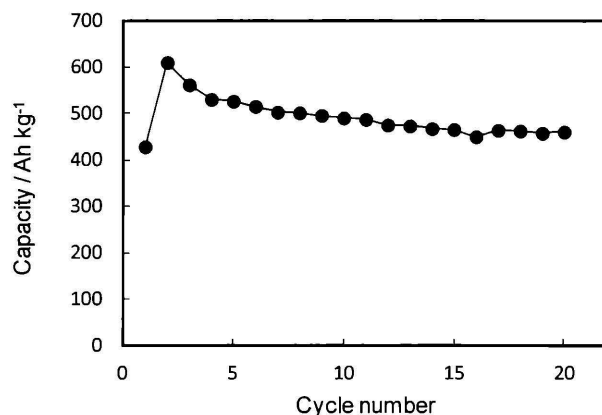


Fig. 12 Discharge capacity vs. charge/discharge cycle number of rubeanic acid half cell. Electrolyte: $\text{LiTFSI}/\text{tetraglyme}$.

As is shown in this figure, the first discharge is composed of single-step process with a voltage plateau of 1.9 V and has a capacity of 440 Ah/kg, which is close to that calculated as a two-electron process. After the second cycle, the capacity increased to 600 Ah/kg and the charge and discharge voltage rised to 2.2 V. The observed large discharge capacity indicates the reaction process with two or more electron contribution.

Figure 12 plots the discharge capacities against the charge and discharge cycle numbers. The high capacities over 450 Ah/kg were maintained during at least 20 cycles.

4. CONCLUSIONS

We have confirmed the battery operations based on the multi-electron reaction of organic compounds. The multi-electron redox-based organic batteries gave high capacities over 400 Ah/kg, which were much larger than those of Li-ion batteries, and the observed maximum capacity was 450 Ah/kg, which was observed for rubeanic acid. It is also an important finding that proper molecular design and proper selection of the electrolyte is important to increase the stabilities of the electrode-active organic materials.

Further development of organic compounds and their multiple electron behavior will lead to a discovery of a new electrode-active material with higher capacity for higher energy density batteries..

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